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REACTIONS OF DIPHENYLCYCLOPROPENONE WITH N-SULFINYLAMINES IN THE PRESENCE OF NICKEL TETRACARBONYL

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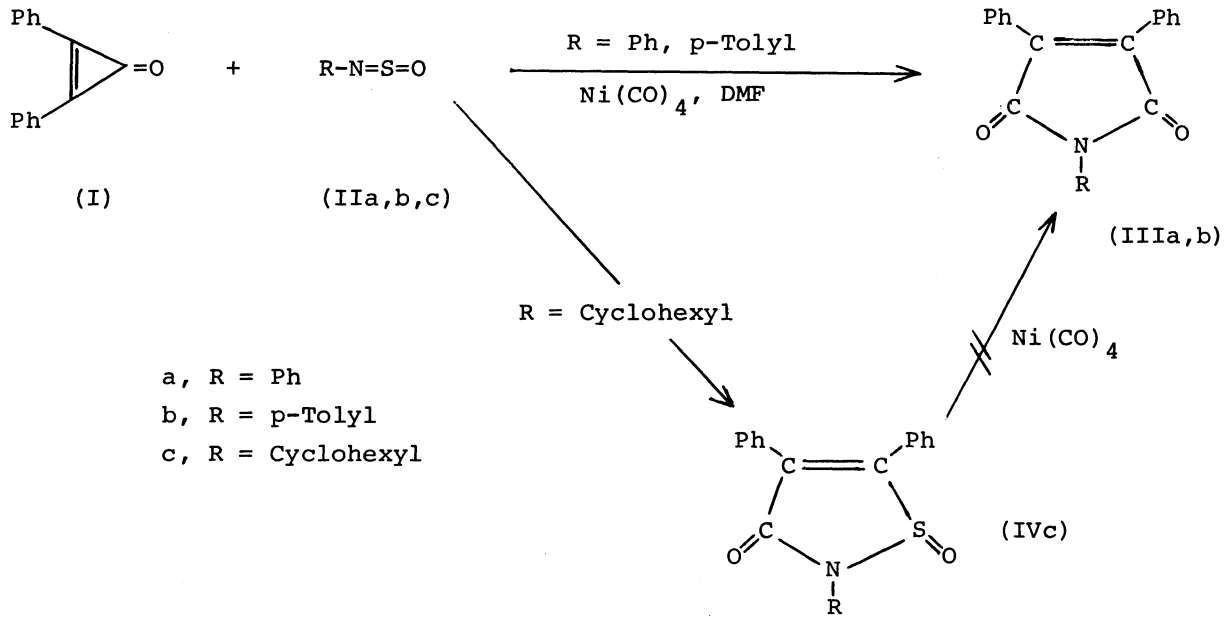
The reactions of diphenylcyclopropenone with N-sulfinylanilines in the presence of nickel tetracarbonyl gave pyrrolines, 1,3,4-triphenylpyrroline-2,5-dione (IIIa) and 1-p-tolyl-3,4-diphenylpyrroline-2,5-dione (IIIb). In these reactions, exchanges of C=O for S=O were observed. On the other hand, the reaction with N-sulfinylcyclohexylamine gave a 1:1 cycloadduct, 2-cyclohexyl-4,5-diphenyl-3-isothiazolone-1-oxide (IVc) in 36% yield without an exchange.

It is well known that diphenylcyclopropenone formes a nickelacyclobutenone complex with nickel tetracarbonyl[1]. Heterocumulenes except activated isocyanates[2] did not react with diphenylcyclopropenone without catalyst. In this paper we wish to report on the reactions of diphenylcyclopropenone with N-sulfinylamines in the presence of nickel tetracarbonyl.

The reaction of N-sulfinylaniline with diphenylcyclopropenone in the presence of nickel tetracarbonyl gave the pyrroline-2,5-dione (IIIa) in 78% yield (reaction temp., 60-65°C; reaction time, 3 hr; solvent, DMF.): green-yellow needles; m.p. 184-185°C (lit.[3] 178-179°C); ir(Nujol) 1760 and 1700 cm^{-1} (C=O); mass 325 (M^+); nmr($CDCl_3$) δ 7.1-7.65 (aromatic protons): Analysis found: C, 81.31; H, 4.58; N, 4.32. Calcd. for $C_{22}H_{15}O_2N$: C, 81.21; H, 4.65; N, 4.31. The product IIIa may be regarded as a 1:1 cycloadduct of diphenylcyclopropenone and phenyl isocyanate, and the latter may be produced by exchange of C=O of nickel tetracarbonyl for S=O of N-sulfinylaniline. However, the reaction with phenyl isocyanate in the presence of nickel tetracarbonyl gave only the trimer of the isocyanate quantitatively, and gave no pyrroline derivative under the same conditions. From this result, we assume that the exchange occurred before the formation of the product IIIa via a metal complex V and phenyl isocyanate did not take part in this reaction. An equimolar amount of nickel tetracarbonyl was necessary, and solvent effect was significant. DMF was the most suitable solvent.

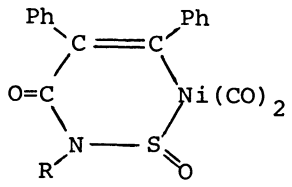
The reaction of N-sulfinyl-p-toluidine with diphenylcyclopropenone gave a similar product IIIb in 42% yield: green-yellow needles; m.p. 193-194°C; ir(Nujol) 1765 and 1700 cm^{-1} (C=O); mass 339 (M^+); nmr($CDCl_3$) δ 7.1-7.6 (aromatic protons) and 3.1 (s, CH_3); Analysis found: C, 81.02; H, 4.77; N, 4.06. Calcd. for $C_{23}H_{17}O_2N$: C, 81.39; H, 5.05; N, 4.13.

In these reactions, 1:1 cycloadducts without the exchanges of C=O for S=O were not obtained.



In contrast with these results, the reaction with N-sulfinylcyclohexylamine gave a 1:1 cycloadduct, 2-cyclohexyl-4,5-diphenyl-3-isothiazolone-1-oxide (IVc), in 36% yield: pale yellow needles; m.p. 183-184°C; ir(Nujol) 1685 (C=O) and 1085 cm^{-1} (S=O); mass 351 (M^+); nmr($CDCl_3$) δ 7.12-7.48 (m, 10H, aromatic protons), 4.00-4.44 (m, 1H, NCH), 1.00-2.36 (m, 10H, $-(CH_2)_5-$); Analysis found: C, 71.51; H, 6.02; N, 4.05; S, 9.06. Calcd. for $C_{21}H_{21}O_2NS$: C, 71.78; H, 6.01; N, 4.05; S, 9.10. An exchanged product was not isolated in this reaction.

In the reaction of the isolated IVa[4] with $Ni(CO)_4$ in the same conditions, the formation of IIIa was not observed and the IVa was recovered. From this result, it was concluded that the exchange of C=O for S=O was proceeded before the formation of IVa. We postulated the intermediate, the metal complex V.



(V)

In all reactions diphenylacetylene was obtained as a by-product in low yields. The acetylene would be produced from diphenylcyclopropenone by decarbonylation. The reaction of diphenylcyclopropenone with $Ni(CO)_4$ was carried out in anhydrous DMF and diphenylacetylene was obtained in 28% yield.

REFARENCES

1) G. Ayrey, C. W. Bird, and E. M. Briggs, Organometal. Chem. Syn., 1 (1970/71) 187.
2) L. A. Paquette, T. J. Barton, and N. Horton, Tetrahedron Lett., 5039 (1967).
3) J. V. Scudi, and H. G. Lindwall, J. Amer. Chem. Soc., 57 2302 (1935).
4) 2,4,5-Triphenyl-3-isothiazolone-1-oxide (IVa) was produced in the reaction of diphenylcyclopropenone with N-sulfinylaniline in the presence of $Fe(CO)_5$ in 21% yield: m.p. 159-160°C; ir(Nujol) 1700 and 1100 cm^{-1}; mass 345 (M^+); Analysis found C, 73.26; H, 4.26; N, 3.99. Calcd. for $C_{21}H_{15}O_2NS$: C, 73.03; H, 4.38; N, 4.06.

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